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# **Resonance Enhanced Two-Laser Infrared Multiple Photon Dissociation of Gaseous Ions**

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## **Abstract**

Ions trapped in a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer exhibited enhanced infrared multiple photon dissociation (IRMPD) when irradiated sequentially by two carbon dioxide lasers using a novel IRMPD probe/pump photodissociation scheme. A low power pulsed (probe) laser tuned to a resonant infrared absorption band promoted trapped ions to vibrationally excited states, but had insufficient energy to cause photodissociation. Subsequent irradiation of the excited ions with a fixed-frequency, nonresonant, continuous wave (pump) laser induced photofragmentation. Photodissociation spectra were obtained by varying the wavelength of the probe laser and monitoring the extent of photofragmentation. A novel White-type cell which dramatically enhances the effect of the probe laser has been designed and constructed for use with these experiments.

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## Introduction

Ion cyclotron resonance mass spectrometry is a powerful technique for studying the kinetics and mechanisms of gas-phase ion/molecule reactions.<sup>1-3</sup> However, it does possess some limitations which are inherent in any mass spectrometric approach. Perhaps the most serious of these is that mass-to-charge ratio is the only real information which is easily obtained either for ions produced directly by various ion formation schemes<sup>4-6</sup> or ions formed in ion/molecule reactions. Several probes, most importantly collisionally activated dissociation,<sup>7-9</sup> have been developed and applied to obtain further information about ion *structures*. However, in contrast to solution studies, no generally applicable spectroscopic technique (such as NMR, IR, or UV-VIS absorption spectroscopy) is available for the elucidation of gaseous ion structures. General approaches which yield spectroscopic information about gaseous ions and thus can assist in determining ion structures are clearly needed.

Infrared spectroscopy is a useful tool for obtaining structural data for organic and inorganic neutral molecules and ions in solution or the solid state. However, except for recent work on very small ions,<sup>10,11</sup> the technique has not been applied in general to gaseous ions. This is primarily due to the difficulty of containing in a small volume a sufficiently high concentration of positive or negative ions to give measurable absorbances when using either conventional infrared sources or, more recently, infrared lasers. However, the use of indirect methods has made it possible to detect the resonant absorption of infrared radiation by gaseous ions of moderate size.

One such indirect method is ion *photodissociation*. Here resonant absorption of one (or more) photons by an ionic species imparts sufficient energy to the ion to bring about dissociation into fragments. In favorable cases one can follow either the disappearance of parent ions or the appearance of fragment ions as a function of irradiation wavelength and obtain an absorption spectrum (the "photodissociation" spectrum). Using *UV-visible* radiation this approach has been shown to provide important information about the energy levels, dissociation dynamics, and structures of gaseous ions<sup>12-15</sup>.

The first<sup>16</sup> demonstration that relatively low-power CO<sub>2</sub> lasers could be used to produce *infrared* multiple photodissociation (IRMPD) suggested that obtaining infrared spectra of ions was feasible. As demonstrated in a number of early experiments<sup>16,17</sup> this process involves the resonant absorption of one or more IR photons by the ion under study. For ions containing more than about 10 atoms there is a sufficiently high density of vibrational-rotational energy levels that the ion is in a "quasicontinuum" of energy states after (resonant) absorption of the initial photon. In the quasicontinuum the ion can rapidly absorb additional photons *no matter what their energy*, since any IR photon will possess an energy linking two states in the quasicontinuum. Additional photons are absorbed until the ion gains sufficient internal energy to dissociate.

Except for a few isolated examples<sup>16-21</sup> there has been no systematic attempt to use IRMPD to obtain spectra of gaseous ions as an aid in structural identification. This is in part due to the limited tuning range of the standard infrared laser sources (CO<sub>2</sub>, CO, NO), and in part due to the low output power and/or difficulty of operation of other tunable infrared sources such as F-center and tunable diode lasers.

In recent years a major thrust of our research has involved using both continuous wave (cw) and pulsed CO<sub>2</sub> lasers to form and dissociate ions in FTICR mass spectrometers.<sup>22-25</sup> While structural information about isomeric ions has been obtained from *fragmentation products* following IRMPD,<sup>22,23</sup> except for some crude diol ion spectra,<sup>26</sup> the limitations mentioned above have precluded extensive infrared spectroscopic studies. However, a new approach developed in our laboratory promises both to provide improved spectroscopic data when using a CO<sub>2</sub> probe laser and also to extend the IRMPD approach to other wavelength ranges of interest in the infrared region.

The basis of the new method is the use of two lasers to uncouple the (initial) resonant absorption of the first one or two IR photons from the subsequent up-pumping through the quasicontinuum to the dissociation limit. Thus, a low-power tunable laser can be used for probing the resonant absorption spectrum, and a more powerful CO<sub>2</sub> laser (which does not have to be tunable) is then used to drive the photodissociation, resulting in a "probe-pump" experiment. This two laser photodissociation process is shown schematically in Figure 1.

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Two-laser photodissociation of ions is not a totally new concept. Dunbar reported<sup>15,27</sup> enhancement of *visible* photodissociation when ions were first subjected to IR irradiation by a CO<sub>2</sub> laser. His interpretation was that the "hot" ions produced following absorption of one or more infrared photons had a higher cross-section for subsequent absorption of a visible photon than did unexcited ions. He reported one "spectrum" obtained in this way,<sup>27</sup> but did not pursue the work because of the limited tunability of the CO<sub>2</sub> laser. Comparison of the use of a cw versus a pulsed laser for photodissociation has also been made,<sup>28</sup> but both lasers were not used simultaneously to irradiate ions.

Multipass cells are often used in absorption experiments to increase the irradiation path length. One well-known multi-pass arrangement was first described by White<sup>29</sup>, and is based on an optical arrangement using three spherical mirrors. An FTICR analyzer cell was constructed using the "White-type" optical arrangement by incorporating the mirrors as the receive plates of the cell. Both a more standard FTICR cell and the "White-type" cell were used in the two-laser IRMPD experiments described in this paper.

## Experimental

All experiments were performed in a FTICR mass spectrometer using a Nicolet<sup>30</sup> FTMS 1000 data station and a Nicolet prototype 2 tesla superconducting magnet. The vacuum chamber and ICR analyzer cell used for these experiments were designed and built in our laboratory. The 15.2 cm inside diameter (id) vacuum chamber is pumped by two oil diffusion pumps with id's of 15.2 and 10.2 cm. The combined pumping speed as rated by the pump manufacturer is 1000 L/s. With baking at 473 K the background pressure can be maintained below  $2 \times 10^{-9}$  torr as indicated by an (uncorrected) ionization gauge<sup>31</sup>.

The mass spectrometer was operated in broadband mode covering a frequency range from 2.6 MHz to 10 KHz (corresponding to a mass range of ca. 12 to 2000 daltons). Excitation and detection of the ions was accomplished using the standard frequency chirp excitation method. Typically, 200 to 500 time-domain transient signals, each containing 16384 data points, were averaged for each experiment. The averaged

time-domain data were then apodized using a three term Blackman-Harris window function<sup>32</sup> and zero-filled once prior to Fourier transformation.

Ions were formed by conventional electron ionization. A trapping potential of 1-2 volts was used to trap positive ions and a potential of -1 volts was used for negative ions. Higher trapping potentials of ca. 3-5 volts were needed to contain ions in the White-type cell. The electron beam voltage was varied from 9 to 50 volts to form positive ions. Negative ions were formed by electron attachment with a beam of low energy (0.2 volt) electrons. Ions were formed either directly from electron impact/capture ionization or as products of ion/molecule reactions. After ion formation, selected ions were isolated using multiple swept-frequency ejection pulses. The ions were stored in the FTICR analyzer cell for sufficient time (>500ms) such that nonreactive momentum transfer collisions and/or radiative relaxation removed excess internal energy. The event sequence for the two-laser probe/pump experiment is shown in Figure 2. Following the ionization, thermalization and isolation events, the trapped ions were sequentially irradiated with the output of a pulsed CO<sub>2</sub> laser (probe) and a gated cw CO<sub>2</sub> laser (pump). The parent and photofragment ions were detected and the extent of photodissociation was assessed by measuring an increase or decrease in mass spectral peak areas.

A Lumonics<sup>33</sup> model TE 860 CO<sub>2</sub> laser and Apollo<sup>34</sup> model 570 cw CO<sub>2</sub> laser were used as the probe and pump lasers, respectively. The former laser was line-tunable over a wavelength range of 9.10 to 10.82  $\mu\text{m}$ . The output energy of this (probe) laser could be varied from 0.05 to 2 joules, but below 0.05 joules its output became unstable. The laser pulse width was 200  $\mu\text{s}$ , although ca. 5% of the pulse energy was contained in a tail extending an additional 1  $\mu\text{s}$ .

The cw (pump) laser was operated at a constant wavelength and power setting of 10.61  $\mu\text{m}$  and 50 watts, respectively. The output from this laser was controlled by gating on the laser power supply. Typically, this laser was used to irradiate trapped ions for a 50 ms interval. The triggering/gating of each laser was controlled by the FTICR data station.

Irradiation of the ions was facilitated by modifying the standard 2.5 cm cubic stainless steel cell to include holes in an excite plate and a trap plate. As illustrated in

Figure 3, the pulsed (probe) laser was reflected by a gold plated mirror into the cell through a 2.0 cm diameter hole in an excitation plate. Light from the (gated) cw CO<sub>2</sub> laser entered the cell through a 1.25 cm diameter hole in one of the trap plates. This trap plate was covered with a coarse stainless steel mesh of ca. 90% transparency to maintain the required trapping potential. For both laser beams, highly polished cell plates were mounted opposite the plates containing the laser beam entrance holes and served as reflecting surfaces, allowing both laser beams to make a double pass through the cell.

Figure 4 illustrates the White-type cell used for multipass probe laser experiments. The spherical mirrors were machined from brass, highly polished, and serve as the receive plates of the ICR cell. The excite plates were constructed of stainless steel mesh. The pulsed probe laser used for resonant excitation is reflected from a turning mirror and enters the cell through a hole at one end of the single mirror receive plate. The gated cw pump laser used for non-resonant excitation through the quasicontinuum enters the cell via a mesh-covered hole in one of the trapping plates in a manner similar to that used with the more standard two-laser cell described above.

All samples were obtained from commercial sources. Sample purity was confirmed by broadband mass spectral analysis. No additional sample purification was required.

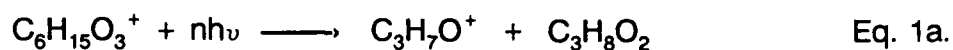
## Results and Discussion

In order to assess the feasibility of the probe/pump technique several important features of this method were investigated. It was necessary to study the vibrational relaxation rate following initial excitation via the probe laser to determine the effect of the delay time between the firing of the two lasers. Another unknown parameter was the minimum photon flux from the probe source needed to produce "enhanced" photodissociation. The most important question, however, was whether use of a low power tunable source used in conjunction with a powerful nonresonant pump laser could, indeed, produce useful photodissociation spectra.

*Vibrational Relaxation.* The rate of vibrational relaxation of protonated bis-methoxy-



diethyl ether (diglyme,  $C_6H_{14}O_3$ ) molecules was studied after initial absorption of photons from the probe laser. The protonated diglyme molecules were formed via ion-molecule reactions of electron impact fragment ions and neutral diglyme molecules present at a pressure of  $5 \times 10^{-8}$  torr. After a 1s reaction time, all ions except the protonated molecule at  $m/z$  135 ( $C_6H_{15}O_3^+$ ) were ejected from the cell. Next an additional 500ms delay was included to allow removal of any excess internal energy by radiative and/or collisional quenching. The protonated parent ions were then irradiated with the output from the probe laser and, after a variable delay period, the pump laser was gated on to induce photodissociation. The  $C_6H_{15}O_3^+$  ion underwent IRMPD to form two fragment ions, at  $m/z$  103 ( $C_5H_{11}O_2^+$ ) and  $m/z$  59 ( $C_3H_7O^+$ ).

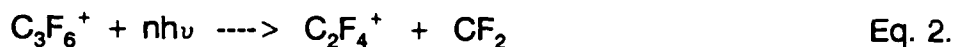


The intensities of the parent and fragment ions were recorded as a function of the delay time between firing of the probe and pump lasers and a plot of these data is shown in Figure 5. Photodissociation was enhanced at shorter delay times and decreased monotonically as the delay time was increased. After about 400ms, the extent of photodissociation reached a constant level consistent with that produced only by the pump laser. At a pressure of  $5 \times 10^{-8}$  torr the initial energy from the pulsed laser had dissipated after about 300 ms, and no IRMPD enhancement was observed at longer delay times. However, at short delay times ( $< 50$ ms) vibrational relaxation of the ion was sufficiently slow that further excitation via the pump laser resulted in "enhanced" IRMPD. Thus, by varying the delay between the probe and pump lasers, a qualitative evaluation of the vibrational relaxation could be made. No attempt has been made to date to extract more quantitative data from these experiments or to assess the degree of collisional versus radiative relaxation.

**Probe Laser Energy.** To examine the feasibility of using probe lasers with modest to low pulse energy for photodissociation studies the extent of "enhanced" IRMPD was measured as a function of the probe laser output energy. Ions investigated were the

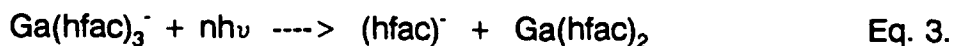
positive molecular ion of hexafluoropropene ( $\text{C}_3\text{F}_6^+$ ) and the negative molecular ion of gallium hexafluoroacetylacetonate ( $\text{Ga}(\text{hfac})_3^-$ ). Neither of these two molecular ions underwent one-laser photodissociation when only the cw (pump) laser was used.

The IRMPD behavior for the  $\text{C}_3\text{F}_6^+$  molecular ion has been previously reported<sup>17,35</sup>. The  $\text{C}_3\text{F}_6^+$  ion undergoes photodissociation via loss of  $\text{CF}_2$  to form the  $\text{C}_2\text{F}_4^+$  ion.



The probe laser was tuned to a resonant IR absorption band of the  $\text{C}_3\text{F}_6^+$  ion at  $9.61 \mu\text{m}$ . Shown in Figure 6 is the extent of photofragmentation observed for the  $\text{C}_3\text{F}_6^+$  in the 2-laser probe/pump experiment and in experiments using only the probe laser. The extent of IRMPD was recorded as the single pulse probe laser energy was reduced from 0.5 to 0.2 joules. The pump laser, at a wavelength of  $10.61 \mu\text{m}$ , induced very little photodissociation when used alone. No photodissociation was observed when only the probe laser was used with output energies below 300 mJ/pulse. However, the probe/pump technique induced photodissociation of the  $\text{C}_3\text{F}_6^+$  ion at probe laser energies well below 300 mJ. Thus, a relatively low power probe source, which cannot induce photodissociation alone, can be used in conjunction with a more powerful pump source to obtain useful photodissociation information.

When the probe laser was tuned to a wavelength of  $9.58 \mu\text{m}$  the negative molecular ion,  $\text{Ga}(\text{hfac})_3^-$  was observed to photodissociate via loss of one of the ligands to form the negative hexafluoroacetylacetonate ion,  $(\text{hfac})^-$ .



When used alone the pump laser ( $\lambda = 10.61 \mu\text{m}$ ) produced no photofragments. The extent of photodissociation for the  $\text{Ga}(\text{hfac})_3^-$  ion is shown in Figure 7 for the two-laser probe/pump experiment and for the one-laser photodissociation experiment using only the probe laser. Little one-laser photodissociation was observed as the energy of the probe laser was reduced below ca. 300 mJ. However, the probe/pump combination

produced "enhanced" IRMPD as the energy of the probe laser was reduced to 50 mJ.

*Wavelength Dependence.* Previous single laser<sup>17,35</sup> studies have shown that the IRMPD spectrum of  $\text{C}_3\text{F}_6^+$  is quite similar to the neutral  $\text{C}_3\text{F}_6$  IR absorption spectrum in the 9.6  $\mu\text{m}$  wavelength region corresponding to a C-F stretching frequency. Similar results were obtained using the 2-laser probe/pump approach. Shown in Figure 8a is the 2-laser IRMPD spectrum of  $\text{C}_3\text{F}_6^+$  obtained by tuning the probe laser wavelength over the range of 9.2 to 10.8  $\mu\text{m}$  at a constant output energy of 250 mJ/pulse and monitoring the production of  $\text{C}_2\text{F}_4^+$ . At this energy level the probe laser has sufficient energy to induce IRMPD. However, when the output energy of the probe laser was reduced to 100 mJ/pulse no IRMPD was observed for  $\text{C}_3\text{F}_6^+$  unless the pump laser was also present, as shown in Figure 8b.

This example illustrates the utility of the probe/pump method. At a probe laser energy of 100 mJ neither the probe nor pump laser alone caused appreciable photodissociation, but when the 2 lasers were used together in a sequential fashion a photodissociation spectrum quite similar to that seen in (higher power) single laser experiments was obtained.

The molecular ion of ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}^+$ , was formed by low energy electron ionization (9.5 eV) and underwent IRMPD with loss of HCl to produce a  $\text{C}_2\text{H}_4^+$  ion. A strong correlation was observed between the IR absorption spectrum of the neutral molecule and the IRMPD spectrum of the chloroethane molecular ion. A comparison of a reduced pressure (200 mtorr) gas-phase neutral IR absorption spectrum obtained on a Fourier transform infrared spectrometer in the Department of Chemistry spectroscopic services laboratory and the IRMPD photodissociation spectrum is shown in Figure 9. The IRMPD spectra obtained by measuring the appearance of  $\text{C}_2\text{H}_4^+$  ions as a function of probe laser wavelength can be seen to be quite similar in appearance to the IR spectrum of the neutral molecule. The P and R branches appear to be much narrower in the IRMPD spectrum, but this probably results from the significant loss of intensity for  $\text{CO}_2$  laser lines as the wavelength is decreased below 10.20  $\mu\text{m}$  or increased above 10.36  $\mu\text{m}$ . Presumably the removal of a non-bonding electron upon ionization of both  $\text{C}_3\text{F}_6$  and  $\text{C}_2\text{H}_5\text{Cl}$  does not alter the vibrational frequencies to an appreciable extent.

*Use of the Multipass Cell.* Enhancement of the IRMPD effect when using the "White-type" ICR cell shown in Figure 4 has been studied in preliminary experiments. Comparison of the results from the multipass cell with those for a double-pass experiment is shown in Figure 10. The  $C_3F_6^+$  IRMPD process represented by Eq. 2 was again monitored. For these experiments only the cw  $CO_2$  laser was used, and it was gated on for increasing time periods to vary the total energy incident on the trapped ions. The results shown in Figure 10 indicate that fragmentation comparable to that seen in a double-pass experiment can be produced in the White cell using laser pulses whose energy is lower by a factor of almost 20.

Although results using the multipass cell in a 2 laser experiment have not been presented, preliminary results indicate that spectra should be obtained with tunable IR sources of much lower pulse energy (on the order of a few mJ) than the 50-200 mJ needed to produce dissociation in the results shown in Figures 6, 7, and 8b. Further cell modifications should also permit ion trapping at lower voltages than the ca. 5 V currently used.

## **Conclusion**

Tunable infrared wavelength sources that by themselves cannot produce photodissociation of gaseous ions can be used in combination with a more powerful pump source to provide valuable spectra. Use of a multipass cell can dramatically lower the energy per necessary from the tunable (probe) laser necessary for IRMPD to be observed. Two laser experiments using the multipass cell are in progress.

## **Acknowledgement**

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## Figure Captions

**Figure 1.** Schematic representation of the two-laser infrared multiple photon dissociation process. Resonant absorption of one or more photons occurs when the probe laser irradiates the trapped ions. The pump laser induces further nonresonant photon absorption resulting in ion dissociation.

**Figure 2.** Event sequence used for the 2-laser probe/pump experiment. After ionization, thermalization, and ion isolation, a low energy pulsed laser resonantly excites the trapped ions and then a powerful nonresonant pump laser induces photodissociation.

**Figure 3.** Cubic ICR cell modified for irradiation of trapped ions. Wire mesh covers the modified trap plate but no mesh was used on the excitation plate.

**Figure 4.** Modified "White-type" multipass FTICR cell configuration. The spherical mirrors used to create the multipass property are incorporated as receive plates.

**Figure 5.** Photodissociation of protonated diglyme as a function of the delay time between the firing of the probe and pump lasers. At short delay times ( $< 5$  ms) 96% of the protonated molecules photodissociate; after 300 ms the amount of dissociation has been reduced to ca. 70%.

**Figure 6.** Photodissociation of the positive perfluoropropene molecular ion as a function of the laser probe energy.

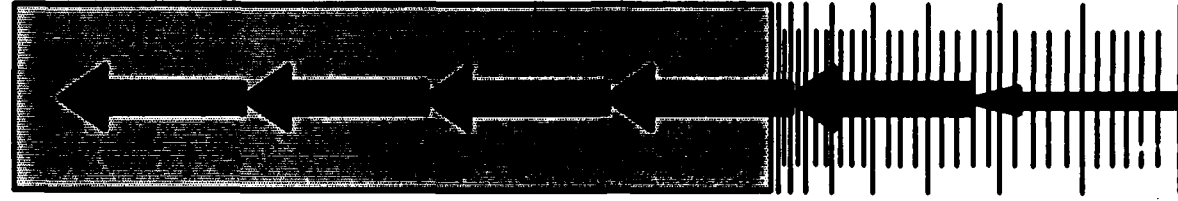
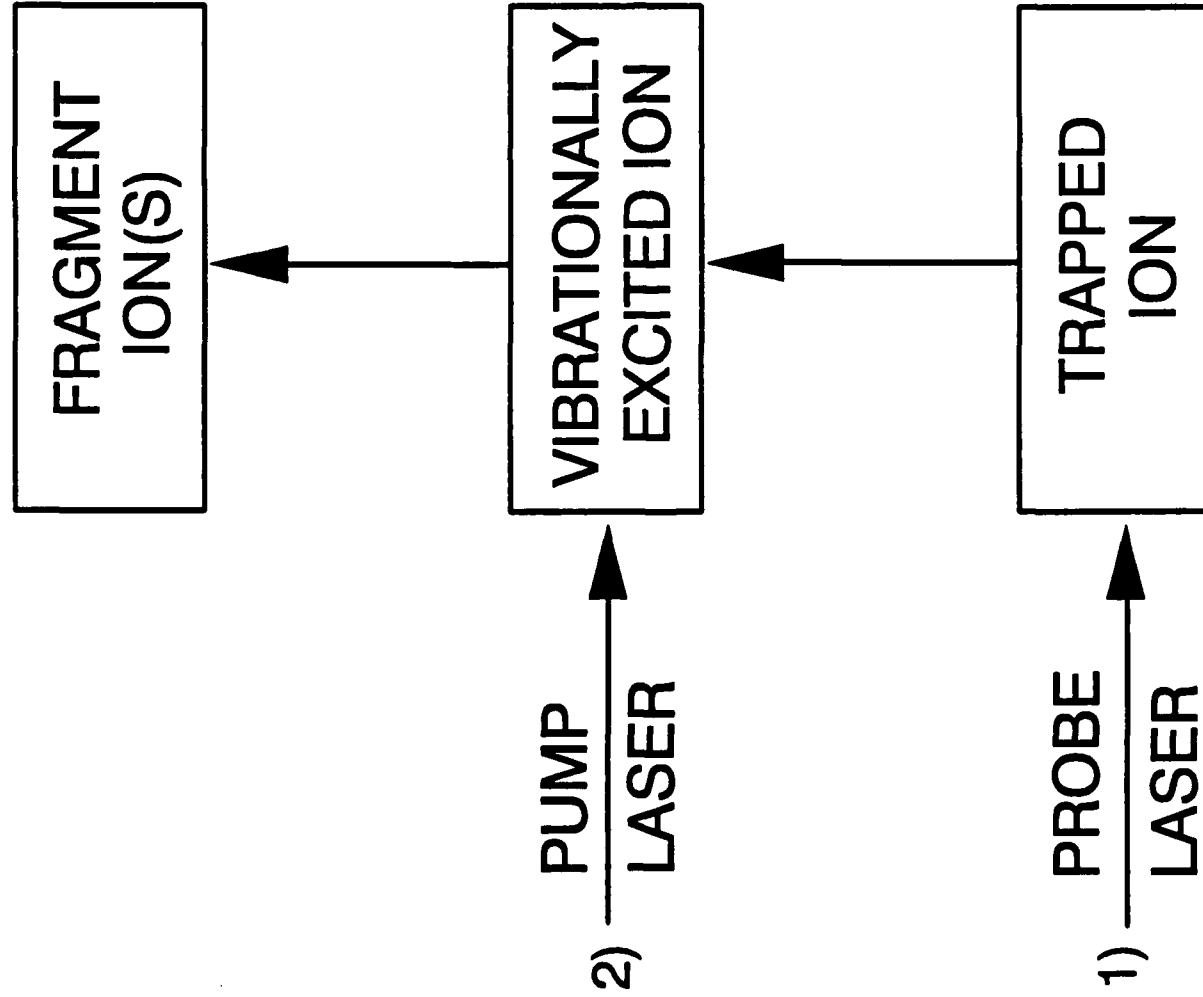
**Figure 7.** Photodissociation of the negative gallium hexafluoroacetylacetonate ion as a function of the laser probe energy. Insert shows an expanded portion at low probe laser energy. Error estimates are 95% confidence limits.

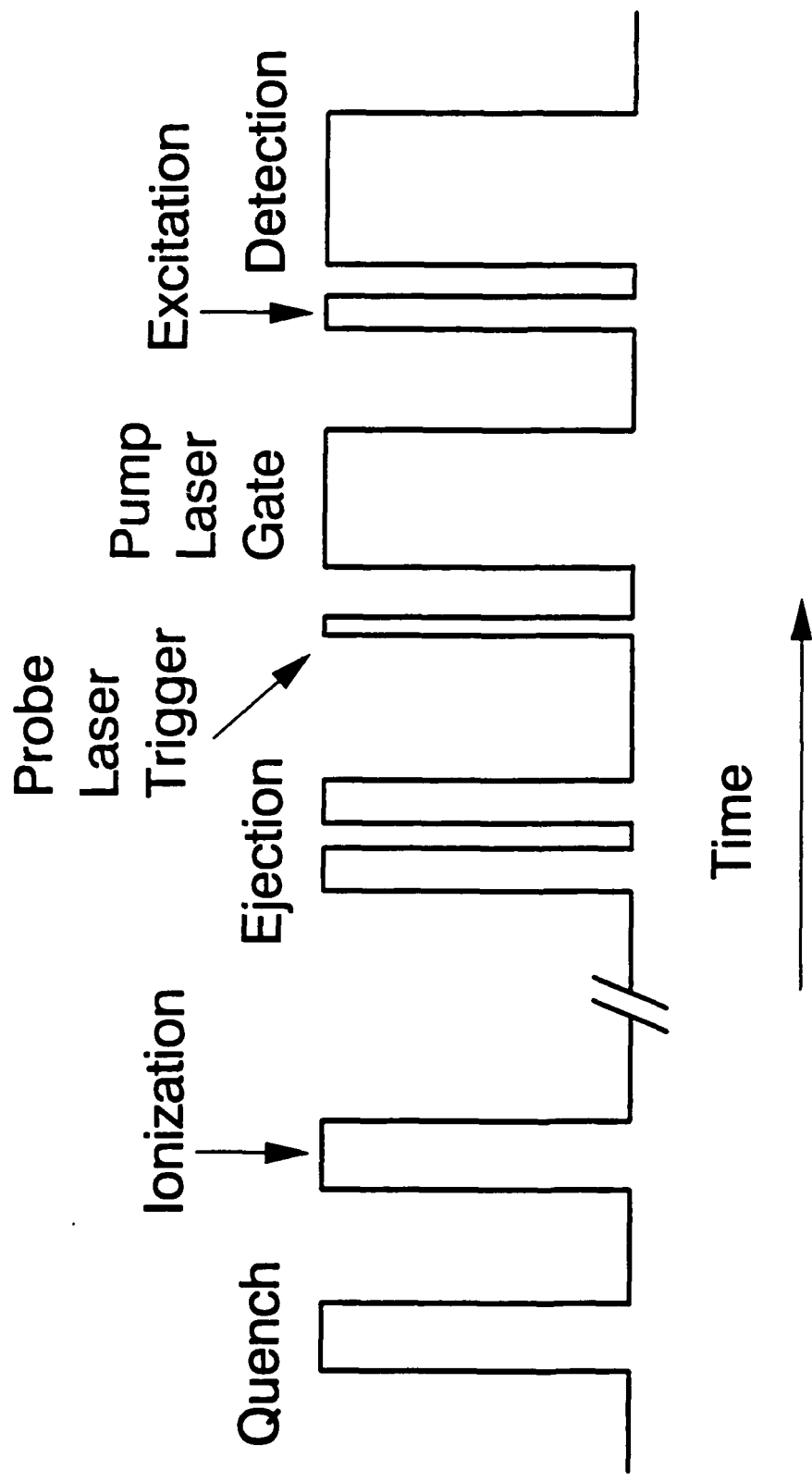
**Figure 8.** a) Photodissociation spectrum for the molecular ion of perfluoropropene at a probe laser energy of 250 mJ. b) Photodissociation spectrum for the molecular ion of perfluoropropene at a probe laser energy of 100 mJ.

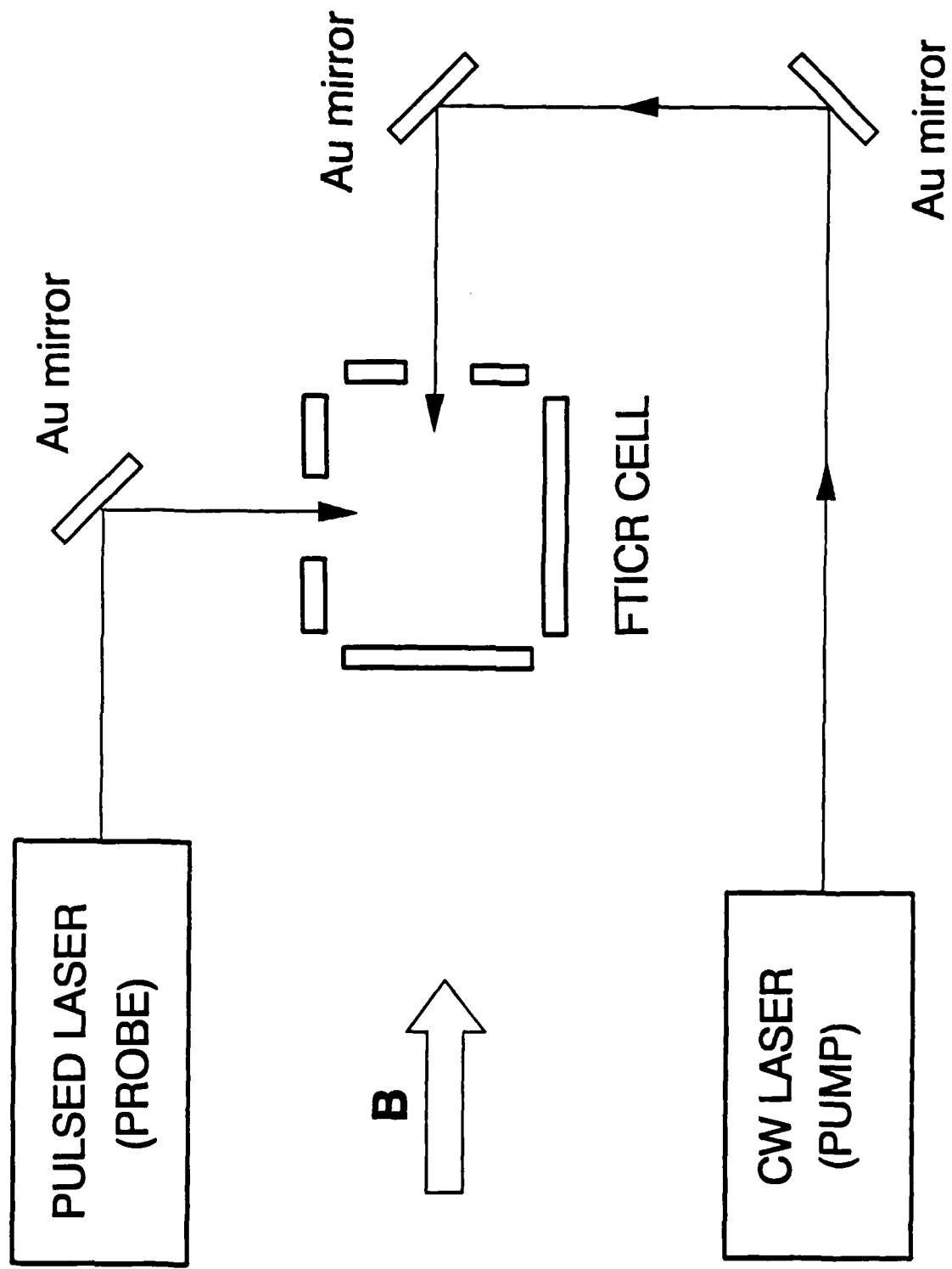
**Figure 9.** Photodissociation spectrum of the positive molecular ion of ethyl chloride compared to the IR absorption spectrum of the neutral molecule.

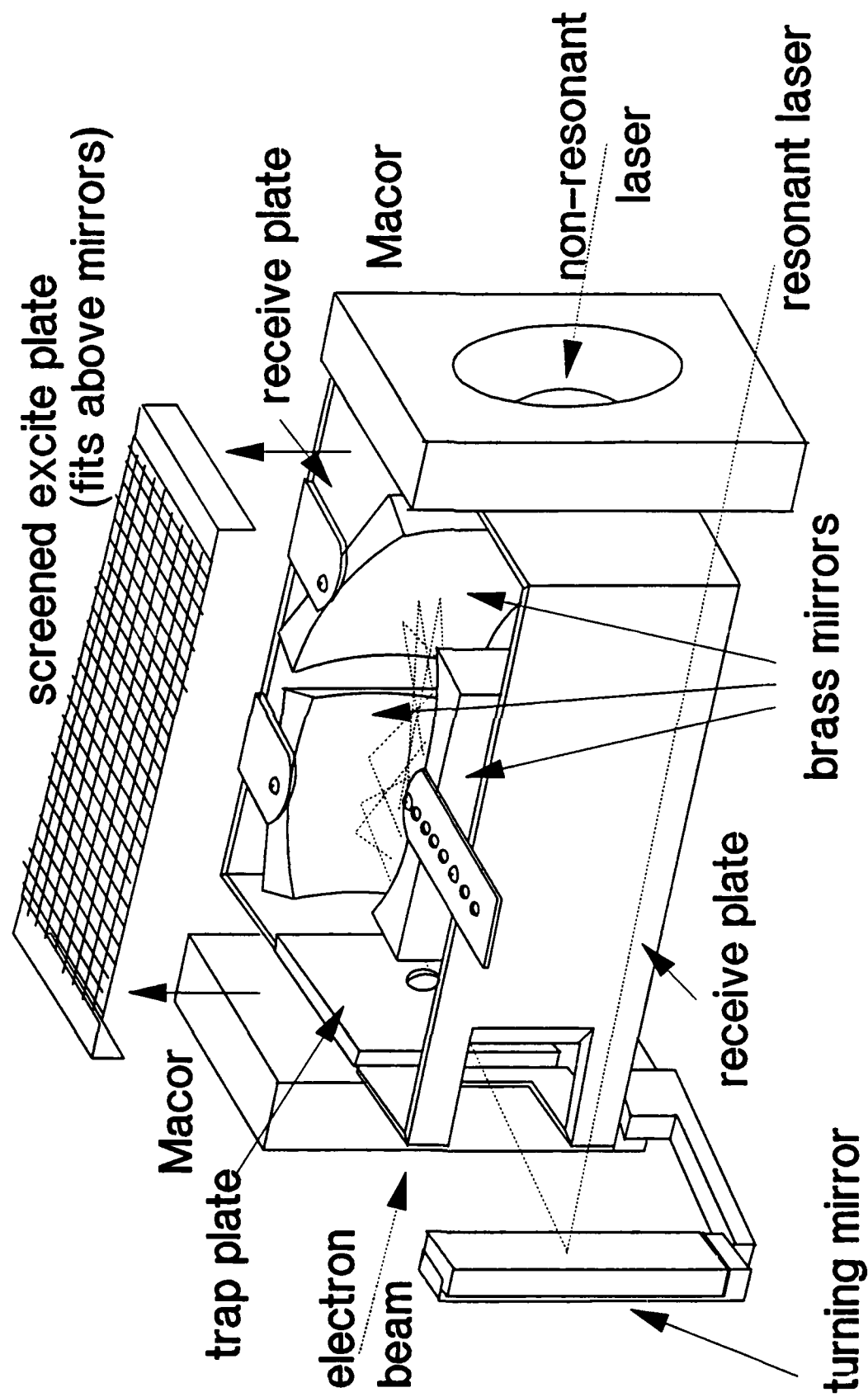
**Figure 10.** Comparison of IRMPD in a multipass "White-type" cell and a standard cubic FTICR cell in which the laser light makes a double pass.

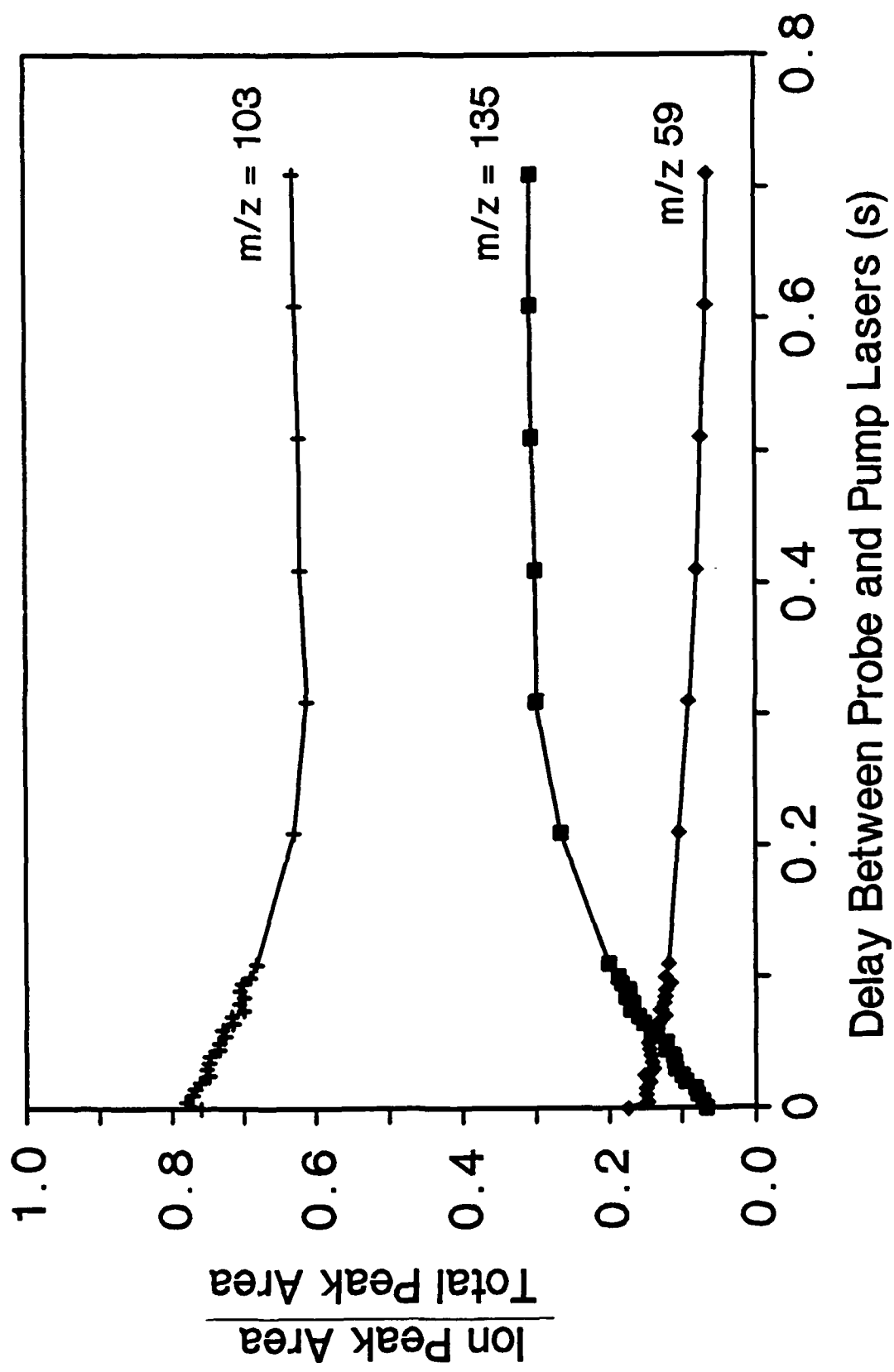


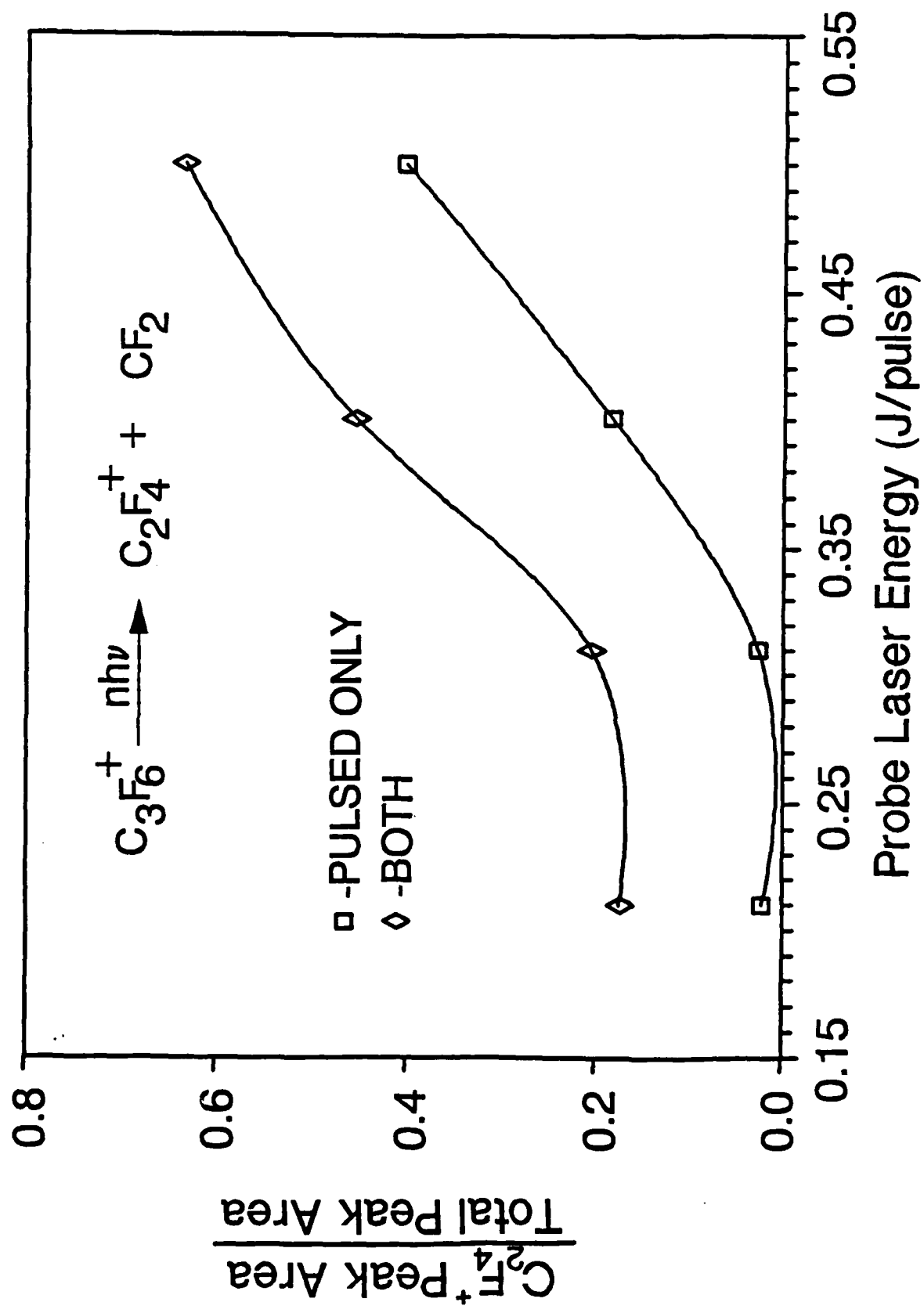


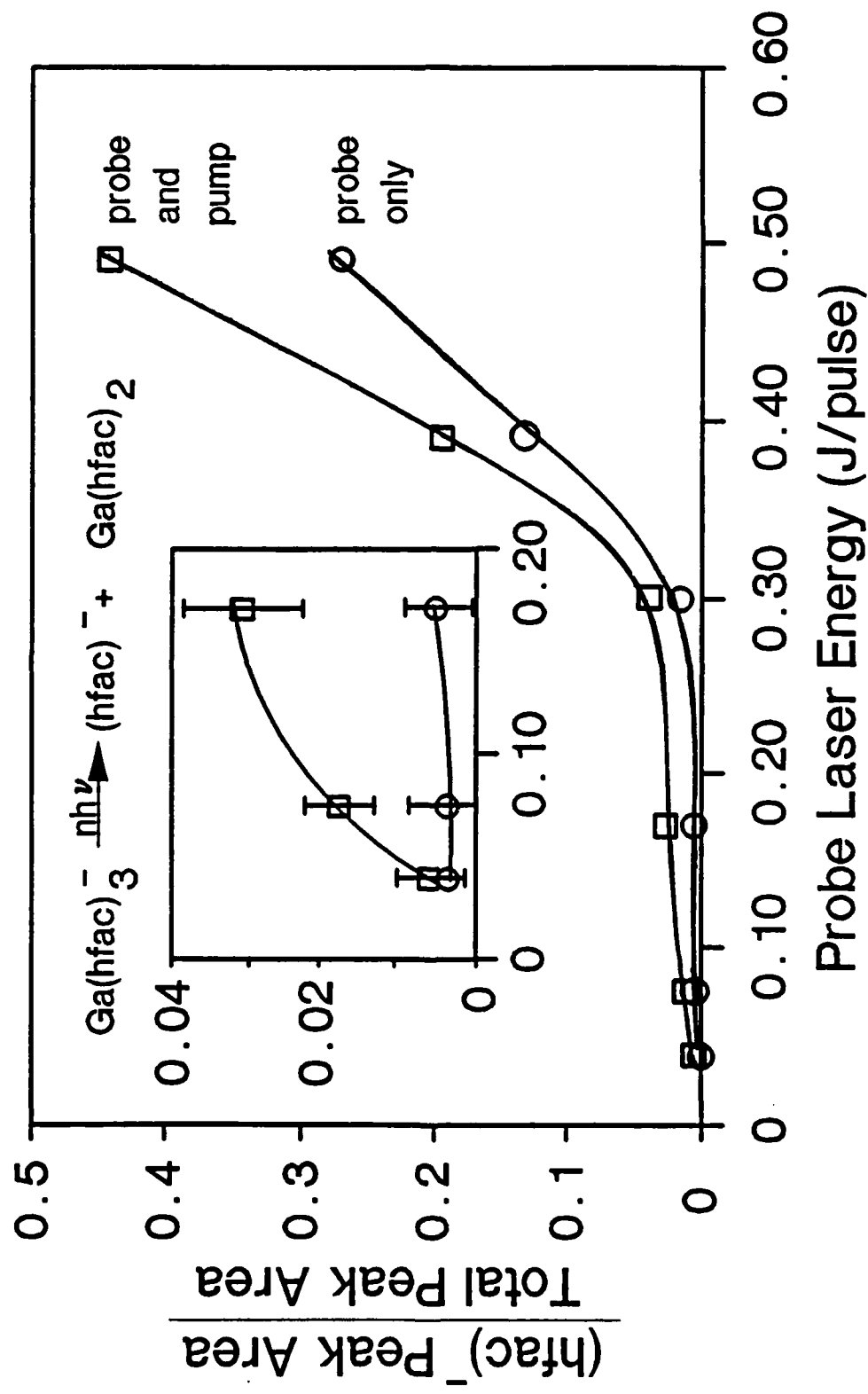


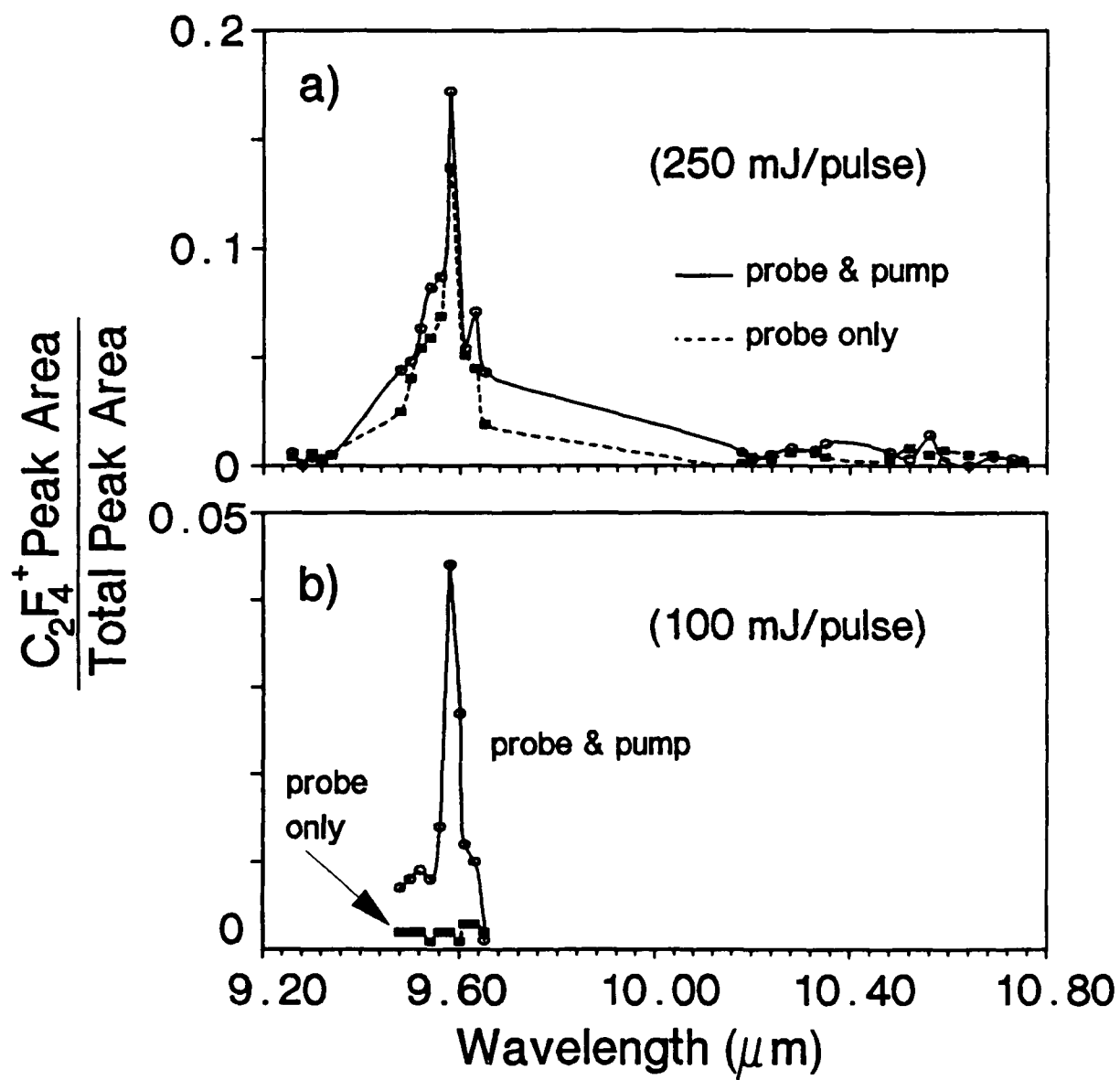




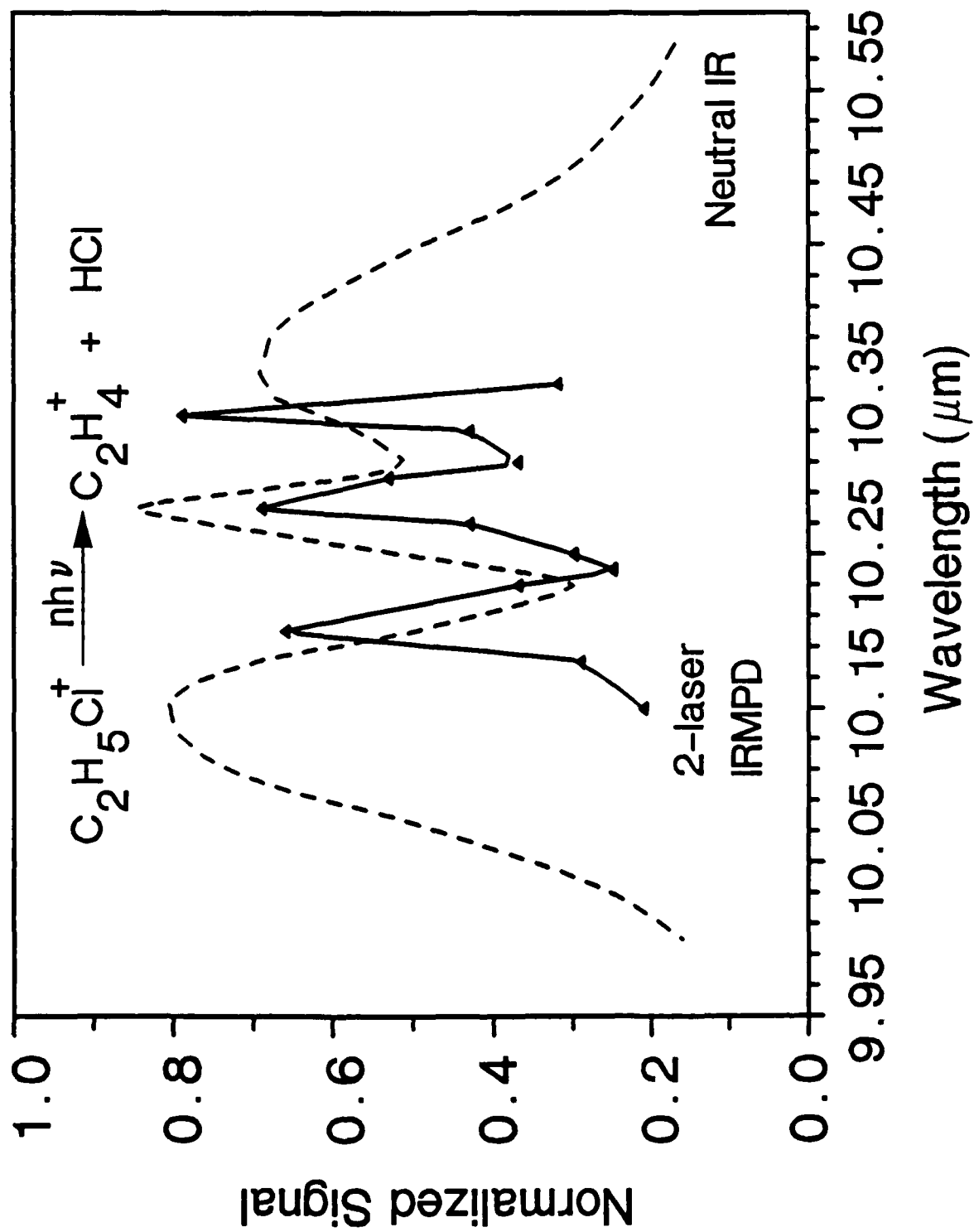


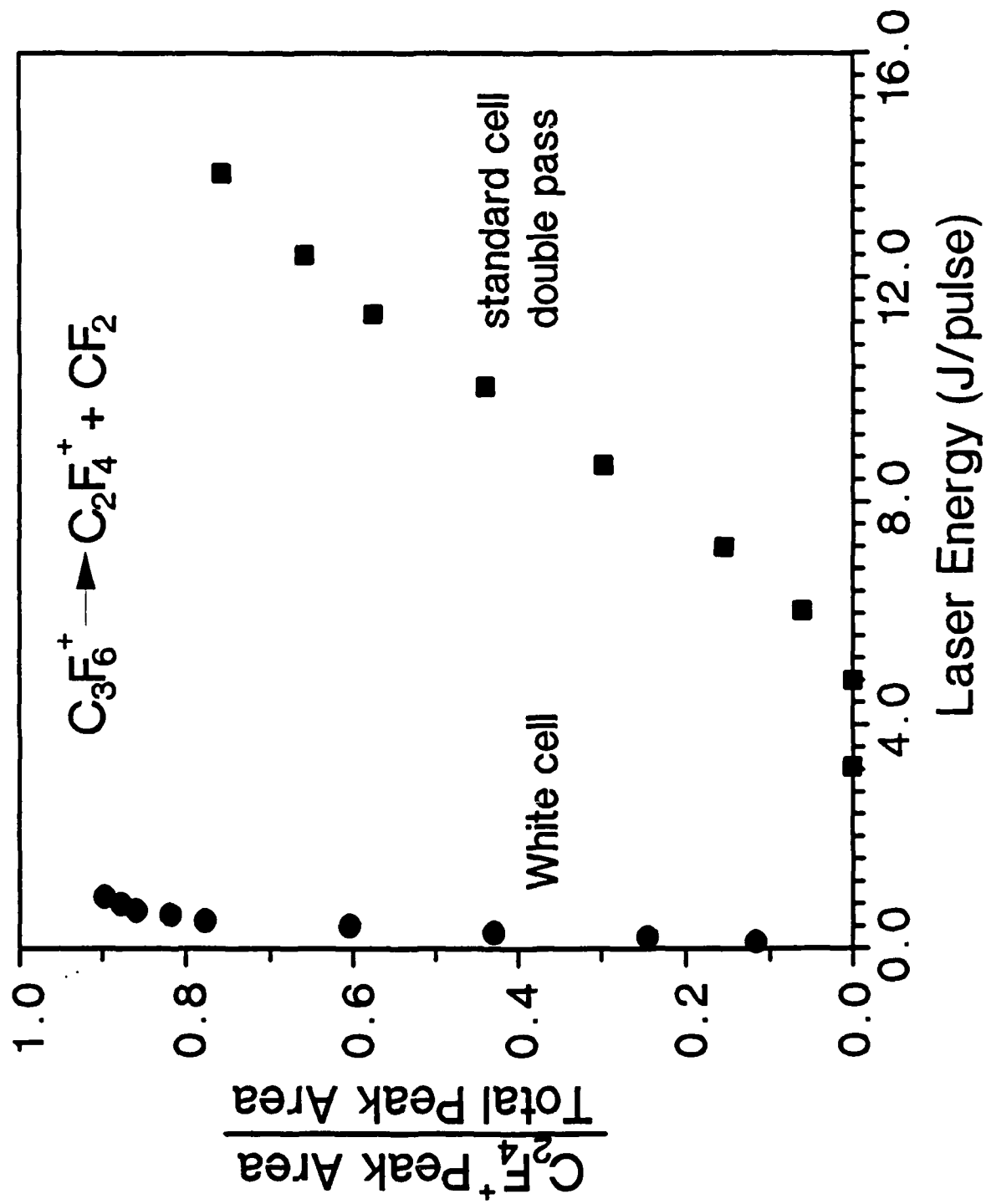












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